# PATENT SPECIFICATION

(11) 1 581 727

(21) Application No. 53352/76 (22) Filed 21 Dec. 1976

(23) Complete Specification Filed 19 Dec. 1977

(44) Complete Specification Published 17 Dec. 1980

(51) INT. CL.[3] B05D 5/00

(52) Index at Acceptance
B2E 1708 423T 426T 438T 466T M

1 581 727

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## (54) COATED MARINE STRUCTURE

(72) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organized under the laws of the Netherlands, of 30, Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to a marine structure, the outer surface of which is at least partly coated with one or more layers, and to a method for the manufacture of such a coated marine structure.

The surfaces of marine structures, such as ships' hulls and buoys, are to be protected against fouling by organisms, such as grasses, algae, barnacles, tube worms, sepula, oysters, ascidia, bryozoa and the like, which fouling occurs when the marine structure is immersed in sea water. The organisms adhere to the surface, and by adding weight and increasing frictional resistance they lead to lower speeds and higher fuel consumption of ships. In order to avoid the necessity of frequent removal of the fouling organisms, coatings for marine structures have been developed which hamper the adherence of the organisms to the marine structure. These coatings comprise paints which contain poisonous substances based upon metals, such as copper, tin, lead, mercury and arsenic. The period over which these paints can prevent fouling is rather limited and moreover in the application of these coatings toxicity problems may be encountered.

Coatings on which the organisms adhere with difficulty, such as silicone resins and silicone rubbers have also been described to have anti-fouling properties, but they do not seem to provide a decisive solution for the fouling problem.

It has now been found that coatings which comprise a vulcanized silicone rubber and a fluid metal-free and silicon-free organic compound, show very attractive anti-fouling and drag-improving properties.

According to the invention there is provided a marine structure, the outer surface of which is at least partly coated with one or more layers, characterized in that the outermost layer is free of silicone oil and comprises a vulcanized silicone rubber together with a fluid metal-free and silicon-free organic compound, which compound is to at least some extent compatible with the said silicone rubber.

Vulcanized silicone rubbers can be prepared from silicone gums, which are highly linear high-molecular weight organosiloxane polymers, consisting essentially of alternating atoms of silicon and oxygen as a polymeric backbone with organic groups attached to the silicon atoms of the polymeric backbone. Vulcanized silicone rubber may be prepared by heat curing with various catalysts (such as peroxides) or by radiation curing of a silicone gum which, e.g., substantially consists of a polydihydrocarbyl siloxane, all or the predominant part of the hydrocarbyl units being methyl units, the remainder being vinyl and/or phenyl units.

Vulcanized silicone rubbers may also be prepared by vulcanizing at ambient temperature silicone gums which contain silanol end groups (the so-called RTV gums). All or the predominant part of the organic groups in the RTV gums in general are hydrocarbyl groups (in particular methyl groups), the remainder may be ethyl-, phenyl- or substituted hydrocarbyl groups, such as chlorophenyl, fluoropropyl or cyanoethyl groups. The use of RTV gum is preferred for the preparation of vulcanized silicone rubbers according to the invention. To prepare a vulcanized silicone rubber from an RTV gum two methods exist.

In the so-called two-package system, the RTV gum may be mixed with a cross-linking

agent, usually ethyl silicate, and if desired, with fillers, pigments, etc. Just before use a suitable catalyst (in general an organic tin-salt, such as dibutyl tin dilaurate or stannous octoate) is blended in, and cross linking starts immediately. It is also possible to add the cross-linking agent and/or the other desired materials partly or totally in ad-mixture with the catalyst to the RTV gum to be vulcanized. Solvents may also be present in one or both of the two components (RTV gum and catalyst) to be mixed.

In the one-package system an RTV gum has been reacted with a compound of general formula $RSiX_3$, in which R stands for hydrocarbyl (in general methyl), and X for a hydroxyl group or a group which contains a hydrolyzable oxygen linkage (e.g., acetoxy) or for an amino group or a group which contains a hydrolyzable nitrogen linkage (e.g., acylamido or ketoxim), or for another reactive site. Solvents, catalysts and/or fillers, pigments, etc., may also be present in the one-package system, which must be kept protected from moisture. Cross-linking occurs when the package is contacted with water, e.g., contacted with a moist atmosphere.

The fluid metal-free and silicon-free organic compound (further also to be called the fluid organic compound) preferably is a compound, or a mixture of compounds, which is liquid at the temperatures prevailing in sea water. It is very suitable that it is compatible with the silicone rubber, which means that a homogeneous mixture can be prepared of the silicone rubber and the amount of fluid organic compound to be incorporated. No significant short term phase separation is to occur before vulcanization, although slow release of the fluid organic compound from the vulcanized silicone rubber, in particular exudation, may occur, and is considered to be of advantage. Very suitable fluid organic compounds are low molecular weight polyolefins (e.g., with a molecular weight up to about 5,000), such as ethylene/propylene copolymers, and in particular polyisobutene, preferably with a molecular weight from 300-500.

Other types of fluid organic compounds very suitable to be used are low molecular weight polydienes, such as polybutadiene and polyisoprene, polyesters, polyisocyanates, polyurethanes and polyepoxides, e.g., polyethylene oxide, polypropylene oxide and copolymers of ethylene oxide and propylene oxide and other oxiranes.

Fluid organic compounds which can also be used are mineral oils and fractions thereof, in particular lubricating oils, such as technical white oils.

The fluid organic compound may also consist of compounds which are indicated as plasticizers. As example of plasticizers may be mentioned esters of carboxylic acids, e.g., of fatty acids, such as lauric acid and stearic acid, esters of dicarboxylic acids, such as adipic acid, azelaic acid, sebacic acid, phthalic acid (e.g., dinonylphthalate) and esters of polyhydric alcohols, such as erythritol. The esters may also comprise hetero-atoms and/or hetero-groups in their hydrocarbon chains which may, e.g., contain hydroxyl groups and/or halogen atoms, such as chlorine, and in particular fluorine, or consist of perfluorinated carbon chains.

Other types of plasticizers which may be used with advantage are phosphorus-containing compounds, such as esters of phosphorus acids, in particular of phosphoric acid (e.g., tricresyl phosphate).

Plasticizers which consist of halogenated hydrocarbons, such as chlorinated or fluorinated hydrocarbons are also very suitable.

It will be understood that the fluid organic compounds to be used according to the invention are not limited to the type of compounds described above. Any fluid organic compound which is compatible to at least some extent with the silicone rubber may be used.

In case the fluid organic compound is compatible with the silicone rubber only in amounts which are not sufficient to ensure a long period of anti-fouling activity, the fluid organic compound is very suitably incorporated in the silicone rubber in an encapsulated form. The material used for the encapsulation is to be slowly permeable for the encapsulated fluid organic compound, so that a low concentration of this compound in the silicone rubber is maintained, enabling exudation of the fluid organic compound from the silicone rubber. The encapsulating material very suitably consists partly or totally of a polymer and may, e.g., be a silicone rubber or other type of rubbery material, or may be based on polyester, polyurethane or cellulose derivatives or any other suitable polymeric material which allows a slow release of the encapsulated fluid into the silicone rubber.

As a matter of course diluents for the fluid organic compounds may be present in the coatings according to the invention. Less effective fluid compounds may be used as diluents or carriers which contain therein only relatively small concentrations of the more preferred fluids.

If desired, materials which enhance the strength of the silicone rubber may also be incorporated. As examples may be mentioned fibrous materials (e.g., glass fibres or nylon fibres) and powdered polymers, such as polytetrafluorethylene.

The amount of the fluid organic compound present may vary between wide limits. Amounts from 0.1 to 100 p.b.w. on 100 p.b.w. of vulcanized silicone rubber are very

suitable.

The fluid organic compound may be applied onto the surface of the marine structure separately or in admixture with a compound which is not a silicone rubber precursor or in admixture with any suitable carrier, and the silicone gum to be vulcanized may be applied on top of it.

However, in applying the coating which comprises the vulcanized silicone rubber and the fluid organic compound onto the surface of the marine structure, it is of advantage to treat the said surface with a mixture which comprises the silicone gum to be vulcanized and the fluid organic compound and to vulcanize the silicone gum in situ. For that reason the fluid organic compound to be used should be of such structure that it does not or only to an insignificant amount take part in the reactions which lead to cross linking of the silicone gum to form a vulcanized silicone rubber.

The invention also relates to a method for the manufacture of a coated marine structure by coating at least part of the outer surface of a marine structure by application of a mixture which comprises a silicone gum and a fluid, metal-free and silicon-free organic compound onto the said surface and vulcanizing the silicone gum.

The silicone gum and/or the fluid organic compound may be applied onto the surface of the marine structure by any suitable means, such as brushing, spraying and the like.

The surface to be coated according to the invention may have been pretreated in order to increase the adhesion of the coating according to the invention thereto, e.g., by sand-blasting and/or application of an adhesive layer. Other coatings may also have been applied, e.g., an anti-corrosive coating and/or an anti-fouling coating of prior art. The coatings according to the invention may also comprise metal-containing anti-fouling agents of prior art.

*EXAMPLES*

Fibre glass panels were coated with a conventional anti-rust system and subsequently with anti-fouling compositions according to the invention with a layer thickness of 150-200 $\mu$. The test panels thus obtained were immersed in sea water at Poole Harbour and their condition was inspected after three and twelve months. The condition of the panels was assessed as they appeared on removal from the water and also following low-pressure water washing. This washing was carried out to obtain an indication of the strength of attachment of the fouling and can be considered to be somewhat analogous to the conditions experienced on a moving vessel.

The panels were rated according to a classification of their degree of fouling, the impact on the final rating being least for slime, and increasing via weed- to crustacea fouling.

As can be seen from the Table the panels of examples 1-8 according to the invention after water wash showed less fouling than panels treated with a conventional anti-fouling paint (experiment 9).

Reference is directed having regard to Section 9, subsection (1) of the Patents act 1949 to Patent No. 1,307,001.

*TABLE*

| No. | Composition | p.b.w. | Rating: 3 months' immersion, no treatment | Rating: 3 months' immersion, after water wash | Rating: 12 months' immersion, no treatment | Rating: 12 months' immersion, after water wash |
|---|---|---|---|---|---|---|
| 1 | Silastic RTV 504 *) | 100 | 8 | 9 | 9 | 9 |
| | Polyisobutylene Mol. Wt. 350 | 20 | | | | |
| | Dow Corning RTV Catalyst S $^{\phi}$ | 20 | | | | |
| 2 | Silastic RTV 504 | 100 | 7 | 7 | 3 | 6 |
| | Tri-cresyl phosphate | 20 | | | | |
| | Dow Corning RTV Catalyst S $^{\phi}$ | 20 | | | | |
| 3 | Silastic RTV 504 *) | 100 | 7 | 7 | 4 | 9 |
| | Di-nonyl phthalate | 20 | | | | |
| | Dow Corning RTV Catalyst S $^{\phi}$ | 20 | | | | |
| 4 | Silastic RTV 504 | 100 | 7 | 7 | 3 | 6 |
| | Eicosafluoro-undecanol ester of branched $C_{10}$ carboxylic acid | 0.2 | | | | |
| | Technical white oil, viscosity 75 cS at 100°F | 10 | | | | |
| | Dow Corning RTV Catalyst S $^{\phi}$ | 20 | | | | |
| 5 | Silastic RTV 504 *) | 100 | 4 | 7 | 3 | 6 |
| | Branched octanol ester of perfluoro octanoc acid | 0.2 | | | | |
| | Technical white oil, viscosity 75 cS at 100°F | 10 | | | | |
| | Dow Corning RTV Catalyst S $^{\phi}$ | 20 | | | | |

*) Silastic (Registered Trade Mark) RTV 504 is a commercial silicone gum. $\phi$ Dow Corning (Registered Trade Mark) RTV Catalyst S, a commercial catalyst, is a paste which contains dibutyltin dilaurate; the cured silicone rubbers contain 0.66%w tin.

*TABLE (cont'd)*

| No. | Composition | p.b.w. | Rating: 3 months' immersion, no treatment | Rating: 3 months' immersion, after water wash | Rating: 12 months' immersion, no treatment | Rating: 12 months' immersion, after water wash |
|---|---|---|---|---|---|---|
| 6 | Silastic RTV 504 *) | 100 | 4 | 7 | 4 | 9 |
| | Polyisobutylene Mol. Wt. 350 | 10 | | | | |
| | Eicosa fluoro undecanol ester of branched $C_{10}$-carboxylic acid | 0.2 | | | | |
| | Dow Corning RTV Catalyst S $\phi$ | 20 | | | | |
| 7 | Silastic RTV 504 *) | 100 | 4 | 7 | 3 | 6 |
| | Technical white oil, viscosity 75 cS at 100°F | 20 | | | | |
| | Dow Corning RTV Catalyst S $\phi$ | 20 | | | | |
| 8 | Silastic DC 9161 RTV silicone rubber **) | 100 | 7 | 9 | 6 | 9 |
| | Technical white oil, viscosity 75 cS at 100°F | 12 | | | | |
| | Dow Corning N 9162 Catalyst $\phi\phi$ | 3 | | | | |
| 9 | Commercial long life anti-fouling paint | | 6 | 6 | 5 | 5 |

*) Silastic (Registered Trade Mark) RTV 504 is a commercial silicone gum.

$\phi$ Dow Corning (Registered Trade Mark) RTV Catalyst S, a commercial catalyst, is a paste which contains dibutyltin

**) Silastic (Registered Trade Mark) DC 9161 RTV silicone rubber is a commercial silicone gum.

$\phi\phi$ Dow Corning (Registered Trade Mark) N 9162 catalyst is a commercial catalyst.